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van Doren, H.A.; Galema, S.A.; Engberts, J.B.F.N.

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Notes

Unexpected Formation of Vesicular Aggregates in Aqueous Solutions of *n*-Octyl 1-Thio- α -D-talopyranoside. Marked Effects of Intramolecular Hydrogen Bonding

Henk A. van Doren,^{*,†} Saskia A. Galema,^{‡,1} and Jan B. F. N. Engberts[‡]

Netherlands Institute for Carbohydrate Research (NIKO-TNO), Rouaanstraat 27, 9723 CC Groningen, The Netherlands, and Department of Organic and Molecular Inorganic Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

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Carbohydrate-derived amphiphiles are the subject of intensive investigations, mainly due to their potential as biodegradable, nontoxic, and nonallergenic surface-active components of detergent formulations,² pharmaceuticals, and foodstuffs.

Our interest is focused on the relationship between molecular structure and physical properties of nonionic carbohydrate-derived amphiphiles. In contrast to ionic amphiphiles, the type of aggregate formed in aqueous solution changes upon chain elongation.³ We have established a firm relationship between the number of hydrogen-bond-forming functionalities in the headgroup and the type of aggregate that is formed in aqueous solution at a given alkyl chain length.⁴ This theory predicts that hexopyranose derivatives with a single alkyl chain up to at least *n*-nonyl will form micelles in solution. However, this approach cannot predict the differences that may arise from variation in carbohydrate stereochemistry.⁵ To study the influence of the stereochemistry of the headgroup, several novel alkyl 1-thioglycopyranosides have been synthesized.⁶ Relatively short (*n*-hexyl to *n*-octyl) alkyl chains were chosen to avoid solubility problems.

Lyotropic behavior can be screened conveniently with the aid of the contact preparation method.⁷ We found that *n*-heptyl 1-thio- α -D-glucopyranoside⁸ forms normal hexagonal (H_I), bicontinuous cubic (V_I), and fluid lamellar (L_α) phases as a function of increasing surfactant concentration, as anticipated on the basis of elegant work by Chung and Jeffrey.⁹ Lyotropic mesophases result from a packing of the aggregates in aqueous solution into ordered structures. Therefore, the nature of the mesophase at the interface with bulk water (*i.e.*, at maximum hydration)

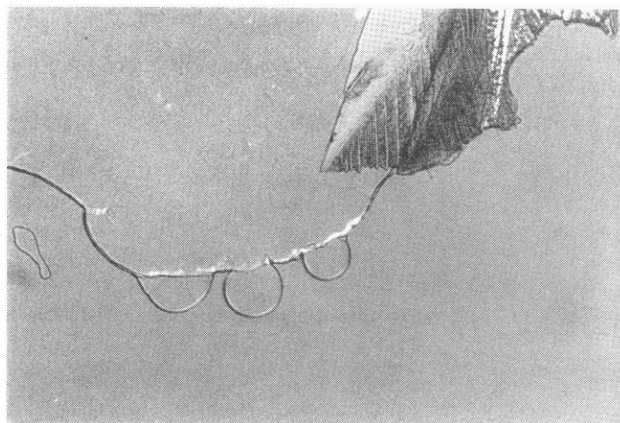


Figure 1. Transient formation of myelin-like protrusions during the penetration of water (bottom) into the supercooled S_{Ad} phase of octyl 1-thio- α -D-talopyranoside (top); photographed at 5 °C; magnification ca. 300 \times . The onset of crystallization is visible in the upper right-hand corner.

should be indicative of the morphology of the aggregates in aqueous solution.⁴ In turn, the morphology of these aggregates is determined by the overall shape of the (hydrated) surfactant molecules.¹⁰ Thus, an H_I -phase (rodlike micelles in solution) contains aggregates of wedge-shaped molecules, whereas the molecules in the L_α -phase are cylindrical in shape (vesicular aggregates in solution). The V_I -phase represents an intermediate situation.

The alkyl 1-thio-*b*-D-glucopyranosides were too soluble at ambient temperature to observe any lyotropic phases, but we did obtain an H_I -phase in the case of the *n*-octyl (and lower) 1-thio- α -D-glucopyranosides as well as for the corresponding α - and *b*-D-galactopyranosides.

Quite unexpectedly, the derivatives of their respective C-2 epimers D-mannose (**2**) and D-talose (**1**) display a significantly different type of behavior. All the D-mannose and D-talose derivatives studied, even with an *n*-hexyl chain, form a bicontinuous cubic (V_I) phase at the interface with water. At 25 °C, octyl 1-thio- α -D-talopyranoside (α -**1**) also formed a V_I -phase, but when water was allowed to penetrate the supercooled smectic A phase of α -**1** at a temperature below 20 °C, transient formation of myelin figures was observed (Figure 1). Their formation is consistent with an overall cylindrical molecular shape of the amphiphile at maximum hydration. Consequently the aggregate morphology in aqueous solution has to be lamellar.¹¹ This was indeed borne out in practice. Multilamellar vesicles, prepared by the ethanol-injection method, were observed with both negative staining and freeze fracture electron microscopy. An electron micrograph is shown in Figure 2. By contrast, a similar experiment with octyl 1-thio- α -D-mannopyranoside (α -**2**) did not reveal the presence of vesicles. The solubility of the corresponding *b*-D-mannopyranoside was not sufficient to allow the preparation of a suitable sample for electron microscopy.

Our results indicate that the effective headgroup size at maximum hydration of the talose derivatives is

[†] Netherlands Institute for Carbohydrate Research (NIKO-TNO).

[‡] University of Groningen.

(1) Present address: Unilever Research Laboratories, P.O. Box 114, 3130 AC Vlaardingen, The Netherlands.

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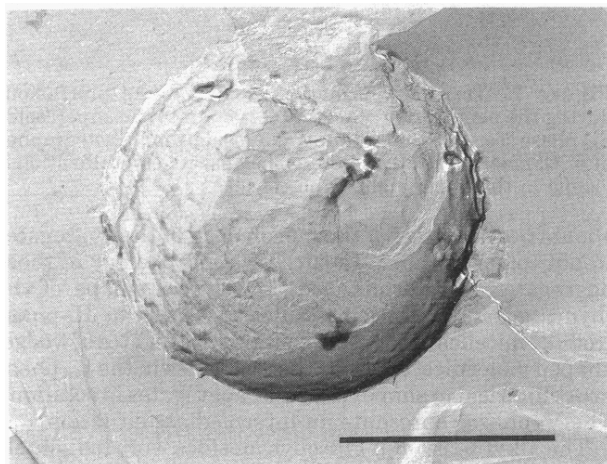
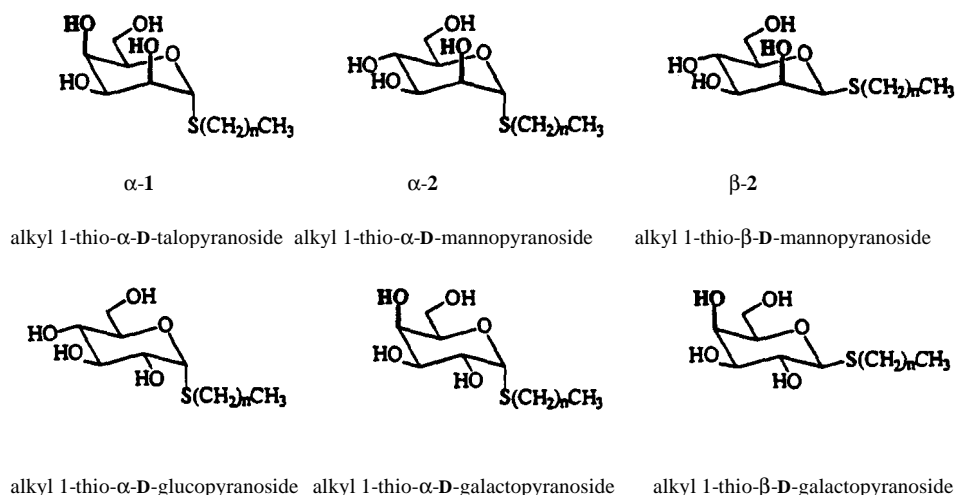


Figure 2. Freeze-fracture electron micrograph of multilamellar vesicles of octyl 1-thio- α -D-talopyranoside: magnification 62000 \times ; bar represents 1 μ m.

significantly smaller than that for similar derivatives of other hexoses. Evidence for the lower hydration number of talose in relation to other monosaccharides was provided previously by thermodynamic¹² and kinetic¹³ measurements. Most likely, an intramolecular hydrogen bond is formed between OH-2 and OH-4. This was indeed observed in the crystal structure of octyl 1-thio- α -D-talopyranoside.¹⁴ We propose that the intramolecular hydrogen bond persists in aqueous solution. A recent molecular dynamics simulation of α - and β -D-talopyranose in aqueous solution also indicated the presence of an

intramolecular hydrogen bond.¹⁵ As a consequence, the effective number of hydroxyl groups available for hydration is reduced. This leads to a situation which is similar to that in 4,6-*O*-octylidene-D-glucopyranose.¹⁶ In the latter molecule two hydroxyl functions are used to link one alkyl chain, leaving only three unsubstituted hydroxyl groups. Indeed, myelin figures have also been observed in contact preparations of this compound.⁸ The α - and β -D-mannopyranose headgroups do not possess a favorable stereochemistry for intramolecular hydrogen-bond formation between two OH moieties. Consequently, the headgroup can be more strongly hydrated and the cross-sectional surface area is enlarged. This situation favors micelle formation rather than vesicle formation.

Vill *et al.*¹⁷ claim that a D-mannopyranoside headgroup is "narrower" (*i.e.*, the cross-sectional surface area is smaller) than a D-glucose or D-galactopyranoside headgroup. This may be the explanation for the observed differences between the D-mannose and the D-glucose/D-galactose derivatives.

The present results provide a striking example of the differences in molecular assembly that may arise from small variations in stereochemistry affecting the hydration of the carbohydrate headgroups. An understanding of the underlying mechanisms should aid the design of amphiphilic molecules for specific purposes, such as detergency and biological activity.

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